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The surface electrical heterogeneity of the membranes with the different degree of cation-exchanger dispersity

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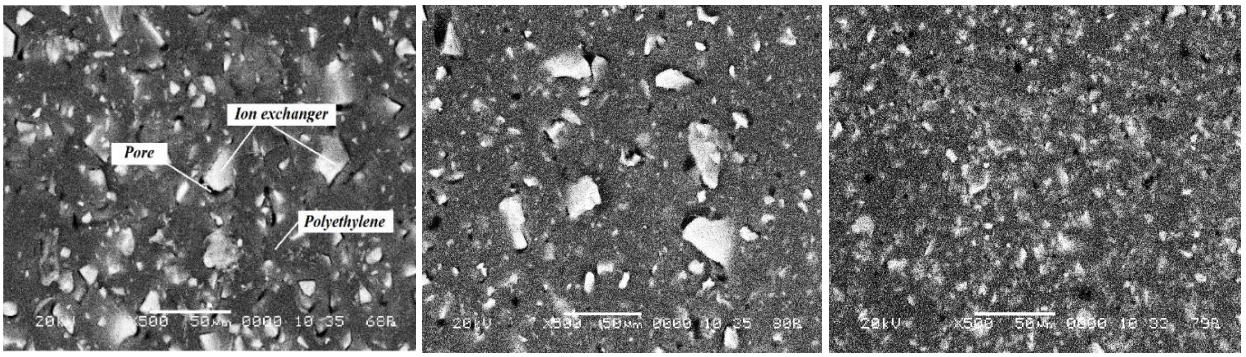
One of the priority tasks of modern membrane electrochemistry and technology is the creation of the ion-exchange membranes with optimized surface for high intensive electrodialysis. The main mechanism for increasing mass transfer in such systems is electroconvection. The purpose of this work is an evaluation of the effect of changing the degree of dispersity of the ion exchanger in the manufacture of the Ralex CM Pes heterogeneous membranes on their surface properties.

In the study there was evaluated the electrical inhomogeneity of experimental samples of heterogeneous cation-exchange Ralex CM Pes membranes (MEGA a.s., Czech Republic) and commercially available MK-40 heterogeneous sulfocation-exchange membrane (LLC "IP Shchekinoazot", Russia). The Ralex membranes were obtained by rolling the homogenised mixture of milled ion-exchanger with varying dispersity degrees with polyethylene. The dispersity degree of sulfocation-exchanger was varied by using of time of its milling from 5 to 80 minutes.

The experimental studies of surface morphology of hydrated and dry membranes were conducted using the method of scanning electron microscopy at JSM-6380 LV microscope (Japan) equipped with regulated pressure, what allows the ion exchange material to be studied under real conditions of its operation (water swollen state). Microphase fractions and sizes were estimated by means of an original software system [1]. The ion-exchange particles dispersity degree *D* was assumed to be the reciprocal of their diameter.

The electrical heterogeneity of the membrane surface is characterized by the proportion and sizes of the conducting regions (ion exchanger particles and pores near them). From the analysis of SEM-images (Fig. 1) of membrane samples, it was found that the proportion of ion exchanger for the heterogeneous sulfocation-exchange membranes is 15-17%.



(a) (b) (c)

Figure 1. Micrographs of the surface of MK-40 (a) and Ralex CM Pes (b, c) sulfocation-exchange membranes in swollen state. Time of ion-exchanger milling: (a) 5 min, (b) 80 min.

Analysis of the distribution of ion-exchange regions along the radii shows that, as compared with the MK-40 membrane, the maximum in the distribution curve for the Ralex CM Pes membrane samples shifts towards smaller values and is in the range of 1-2 μm (Fig. 2). With the increase in the time of ion-exchange particles milling, an increase in their total quantity and a significant increase in the fraction of the ion exchanger with a radius of less than 0.7 μm is established. For membrane samples with the milled ion exchanger for 5 and 80 min, the range of the dispersity degree is $(3 – 80)\cdot10^4$ m^{-1} and $(7 – 125)\cdot10^4$ m^{-1} respectively. For the MK-40 membrane, the range of the degree of dispersity of the ion-exchange resin is $(4 – 60)\cdot10^4$ m^{-1}. With an increase in the degree of dispersity of ion-exchange particles on the surface of swollen samples

of CM Pes membranes, the value of their average radius decreases by 20% and amounts to 1.52 ± 0.03 μm for membranes with the maximum ion exchangers grinding time. According to estimates made in [2], the value of the average radius $\overline{R}$ for the Ralex CM Pes sulfocation exchange membrane that is serially produced by the «MEGA a.s.» company is 1.88 μm.

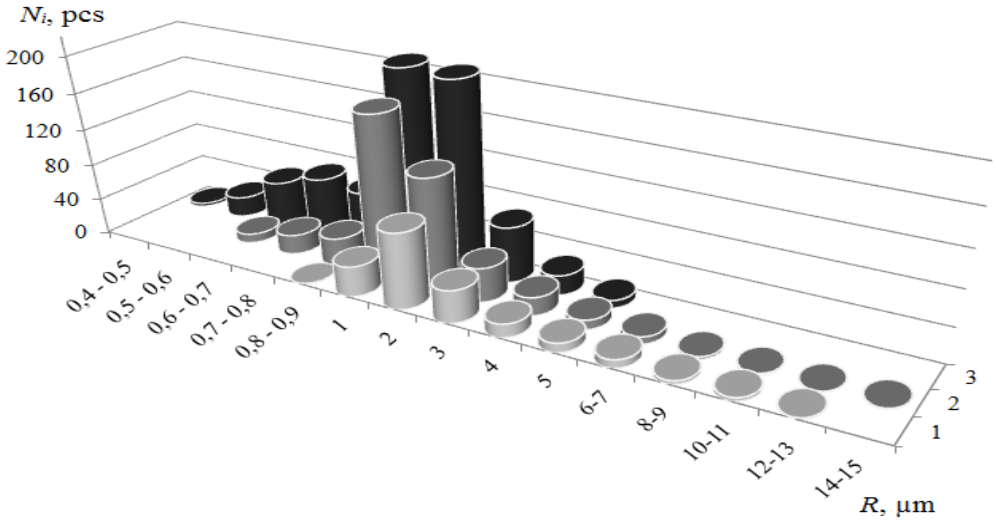


Figure 2. Distribution of ion-exchanger over radii for swollen conditioned samples of MK-40 (1) CM Pes membranes with time of ion-exchanger milling: (2) 5 min, (3) 80 min.

The reduction in the sizes of the ion exchanger regions on the surface of the experimental CM Pes membranes is accompanied by the convergence of the conducting surface zones: the effective distance between the ion exchangers is more than twice and amounts to 9.3 and 5.5 μm for a milling time of 5 and 80 min, respectively.

A significant difference is found between the total surface porosity of CM Pes membranes with the different degree of the ion exchanger dispersity. With increase in time of ion-exchange particles milling from 5 to 80 min, the macroporosity on the surface of the conditioned membranes in the swollen state decreases from 2.5 to 1.8%, wherein the average pore radius values are 1.55 ± 0.03 and 1.27 ± 0.04 μm, respectively.

Thus, the differences in the surface microstructure of the swollen samples of the experimental Ralex CM Pes heterogeneous sulfocation exchange membranes (Czech Republic) with different time of the ion exchanger milling are visualized by the SEM method. The reduction in the size and the convergence of the conducting phase zones, the decrease in the porosity and roughness of the surface of the membranes containing the ion exchanger subjected to a longer milling time are revealed.

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Microphotographs of the membranes surface were obtained at the CCUSE of VSU.

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